A new generation fibre reinforced polymer composites for low and cryogenic temperature applications

A thesis submitted in partial fulfilment of the requirements for the degree of

Master of Technology

In

Metallurgical and Materials Engineering

By

DEVALINGAM SANTHOSH KUMAR

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Department of Metallurgical and Materials Engineering
National Institute of Technology Rourkela
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Under the guidance of

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Department of Metallurgical and Materials Engineering
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CERTIFICATE

This is to certify that the thesis entitled**, "A new generation fibre reinforced polymer composites for low and cryogenic temperature applications"** submitted by Mr. **Devalingam Santhosh Kumar** in partial fulfilment of the requirements for the award of Master of Technology in Metallurgical and Materials Engineering at National Institute of Technology, Rourkela is an authentic work carried out by him under our supervision and guidance. To the best of our knowledge, the matter embodied in the thesis has not been submitted to any other university/institute for the award of any Degree or Diploma.

Date: **Prof. R.K. Prusty** **Prof. B.C. Ray**

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Abstract

In the present investigation, alteration in flexural performance of glass-epoxy (GE) composite and CNT (0.3%)-GE for low temperature and glass-epoxy (GE) composite and CNT (0.1%, 0.3% and 0.5%)-GE composites due to liquid nitrogen conditioning is studied for various time lengths. The epoxy resin is first modified by 0.1% ,0.3% and 0.5% MWCNT, which is then used along with E-glass fibres to fabricate laminate.Flexural strength and modulus were evaluted by 3-point bend test. For low temperature conditioning, addition of 0.3 wt. % MWCNT into GE composite significantly lowered the T_g by 12 °C due to hindrance in crosslink formations. The reinforcement efficiency (relative change in modulus) due to CNT incorporation in GE composite is as high as 30%, when the testing temperature was -80 °C. For cryogenic conditioning, out of these four compositions the maximum strength is as the fabricated conditioned for GE composite with 0.1% CNT, which is 32.7% higher than GE composite. Decrease in strength and modulus observed for short time span of liquid nitrogen conditioning i.e. 0.25hr. Long cryogenic conditions resulted in increment in strength. To understand the failure mechanisms, post failure fractography analysis was carried out using scanning electron microscope. The design parameters are then calculated using Weibull distribution model.

Keywords : Fibre reinforced composite, Flexural properties, Low temperature, cryogenic temperature and Multi walled carbon nanotubes.

Chapter 1

Introduction

1.1 Introduction to composite materials

The word composite means “made up of distinct parts”. Generally, composite materials defined that which materials are made from two or more constituent materials with significantly differ in physical or chemical properties, that when judiciously combined, produce material with superior properties than individual constituents. The main idea of composite materials to make unusual combination of properties for different potential applications. Composite materials are mainly classified into three categories (i) Polymer Matrix Composites (ii) Metal Matrix Composites (iii) Ceramic Matrix Composites. Many composite materials are made of two phases. One is named as matrix, which is continuous phase, other one is reinforced phase.

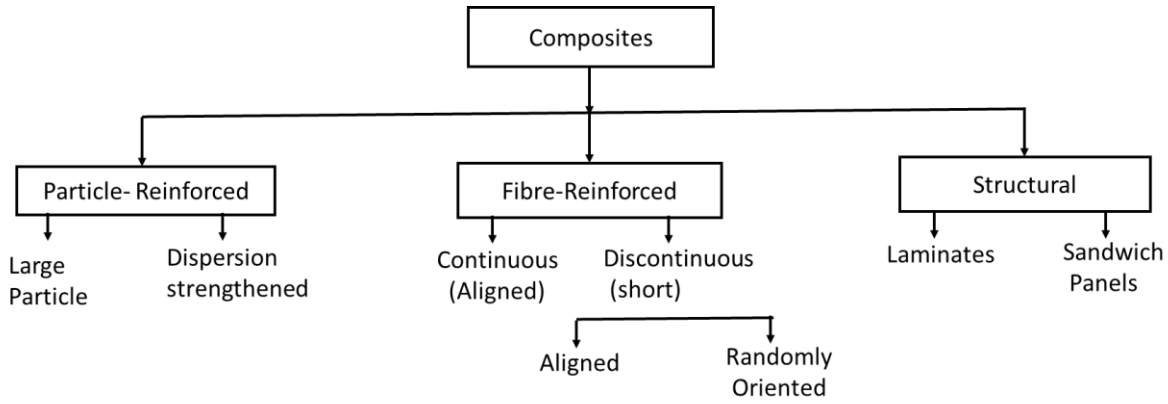

Figure 1.1 Classification scheme for different composite types

Particle Reinforced composites sub classified into two categories, (i) Large particle and (ii) Dispersion strengthened. Commonly used reinforced particles are Aluminium silica, Boron oxide etc. The degree of reinforcement gives the high mechanical properties of the composite. It is depends on strong bonding at the matrix–particle interface. Fibers are usually glass fibres, carbon fibres and aramid fibres.

1.2 Polymer matrix composites

Polymer matrix composites made by combination of one matrix phase and one reinforced phase. Matrix phase ductile in nature. Whereas reinforced in brittle nature.

1.3 The matrix phase

In polymer matrix composites the matrix phase is polymer. The purpose of polymer in PMCs to get a ductile property to composite. Thus, it improves the fracture toughness. In Fibre reinforced composites matrix phase assists several functions. The first function, Polymers binds the fibres together and acts as the medium for stress transfer and distributed to fibres. The second function, matrix act as shied around fibres protect from surface damage. It leads to improve mechanical properties and protect the chemical reactions with environment.

Mainly polymers classified into two types:

(1) Thermo setting polymers

(2) Thermo plastic polymers

1.3.1 Thermo setting polymers

Thermo setting polymers are in state of viscous, during curing it changes irreversibly insoluble polymer network. This process generally called as crosslinking. Thermo setting polymers have high dimensional accuracy. Because of the cross linking, molecules of polymer difficult to move/slide one on another results make it strong and rigid. General examples of thermosetting polymers are epoxy, polyester, polyurethane and silicone.

1.3.2 Thermo plastic polymers

Thermo plastics polymers are gets soften/melt on heating. These polymers mainly suitable for liquid flow forming. Many of thermoplastics polymers having high molecular weight. Intermolecular force acting in between polymer chains, which weaken rapidly with increased the temperature, leads to yielding a viscous liquid. Thermoplastics might be reformed by heating and are typically used to produce different parts by several polymer processing methods such as injection molding, compression molding, calendering, and extrusion. Some examples of thermo plastic polymers are high and low density polyethylene, polystyrene and polymethyl methacrylate (PMMA).

1.4 Fibre reinforced phase

Reinforcement phase is many forms such as flakes, whiskers, short fibre, continuous fibers or sheets. The reinforcements are used in many composites have fibre form it results fibres are stronger and stiffer than any other form. Some examples listed here.

1.4.1 Glass Fibres

Common glass fibres formed by the alumina-borosilicate glass having less than 1% w/w alkali oxides. Many types of glass fibres are there like E-glass, S-glass and C-glass fibres. Here E-significant good electrical insulator also having good strength. S-indicates this glass fibre having high silica. By adding silica to the fibre withstand high temperatures than other glass fibres.

1.4.2 Carbon fibres

Carbon fibres have very light density. Depends on the arrangement of carbon atoms the structure varies. When the carbon atoms arrange in form of three dimensional configuration the structure indicates diamond. The raw material of the carbon fibre is the organic precursor fibres. The carbon fibres having high Young's modulus equal to about 1000 GPa.

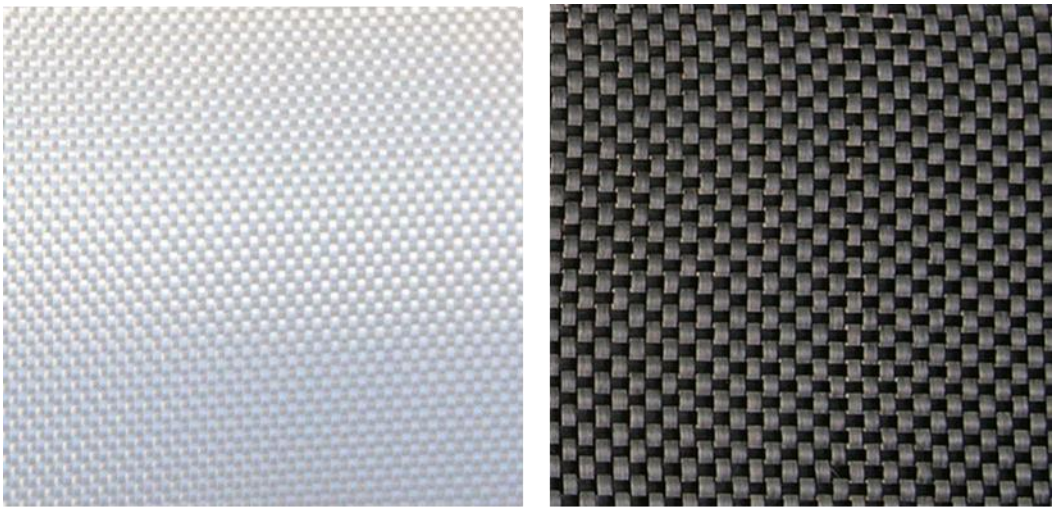

Figure1.2 3K plain weave (a) glass fibre (b) carbon fibre

1.5 Nano reinforcement

Nano particles have nano scale size in geometry. Due to its size these particles have high specific strength. Some of nano fillers listed below.

(i) Alumina

(ii) Silica

(iii) Carbon nanotubes

1.5.1 Carbon nano tubes

A carbon nanotube is a tube-shaped material, made of carbon, having a diameter measuring on the nano scale size. Carbon tubes are formed from the essentially the graphite sheet and the graphite layer appears somewhat like a rolled-up continuous unbroken hexagonal mesh and carbon molecules at the apexes of the hexagon. Depending on the process used for CNT synthesis, CNTs can be classified into single-walled, double walled and multi walled carbon nanotubes.[1] [2].

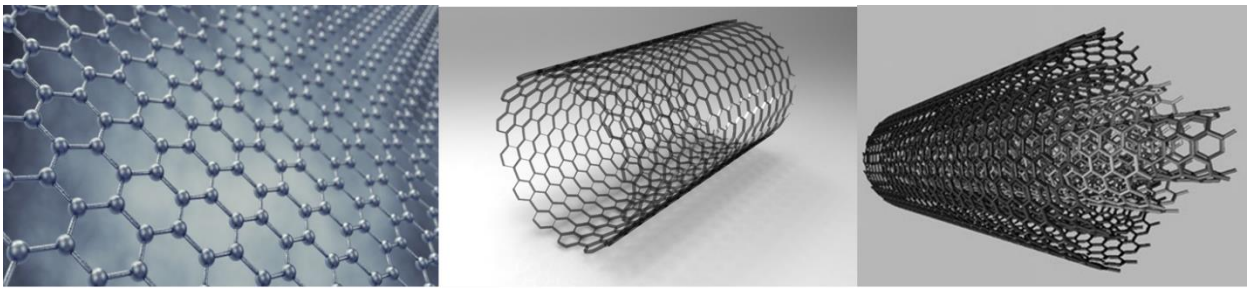

Figure 1.3: Classification carbon nanotubes

Carbon nanotubes have high specific strength and high specific stiffness due to these un paralleled properties fibre reinforced nan composites have become attractive structural materials not only in weight sensitivity aerospace industry but also some functional applications, marine, armour, and automobile applications.[3] [4]. Addition of CNTs in epoxy improves the modulus, stiffness as well as fracture toughness [5] [6].

1.6 Applications of FRP composites

FRP composites find application aerospace industry, marine vehicles, sports goods, structural applications, cryogenic fuel tanks, hydrogen storage tanks, pressure vessels, satellite solar panels, superconducting devices and thermal insulators [7] [8] [9].

Figure1.4: Applications of (a) Fibre reinforced composites (b) carbon nanotubes

1.7 Motivation of the current project

FRP composites have already been proven as trust worthy materials and being used extensively. The main disadvantages in FRP composites are environmental degradation and low impact resistance. This is might be due to poor matrix properties dominated properties. In present work modify the matrix chemistry by adding CNTs to epoxy obtain a superior and reliable material for low and cryogenic temperature applications.

1.8 Objective of the present work

Cryogenic tanks made by conventional materials like aluminium and steel. The main problem finding in conventional metal tanks have continuous propagation of cracks in the primary (inner) containment, leads to sudden dynamic liquid loads being applied to the secondary (outer) containment. The conventional materials have high density, cost and less fatigue resistance than polymer reinforced composites. The composites tanks will be enable the next generation of rocket and spacecraft needed for space applications.

Conventional laminated composites have poor through thickness and poor interlaminar properties. Further at low and cryogenic temperatures the tendency of micro crack generation is higher. Addition of carbon nanotube to the polymer can significantly enhance their matrix dominated properties. CNT is used to modify chemically with a vision to obtain a superior and more reliable material with a less degree of dispersity.

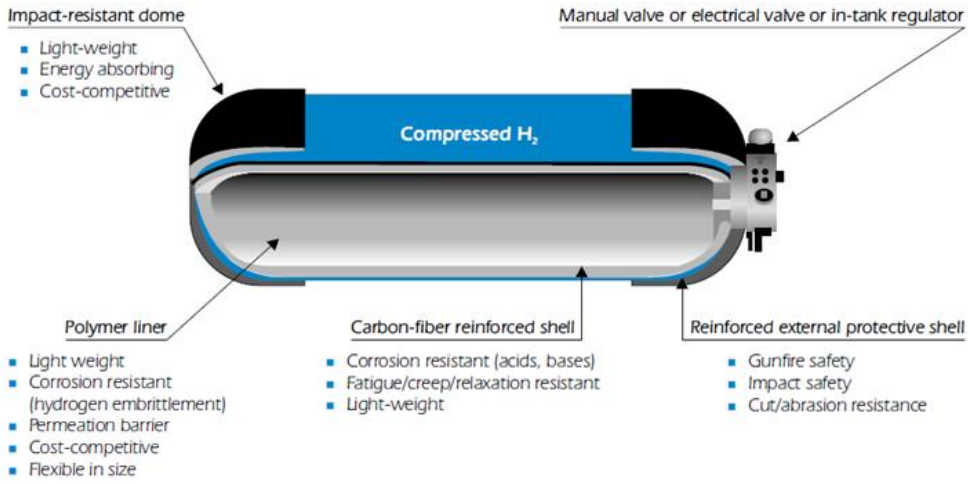

Figure 1.5: Sectional view of compressed hydrogen tank.

References

[1] Allaoui, Aïssa, et al. "Mechanical and electrical properties of a MWNT/epoxy composite." *Composites Science and Technology* 62.15 (2002): 1993-1998.

[2] Baughman, Ray H., Anvar A. Zakhidov, and Walt A. de Heer. "Carbon nanotubes--the route toward applications." *Science* 297.5582 (2002): 787-792.

[3] Biercuk, M. J., et al. "Carbon nanotube composites for thermal management."*Applied physics letters* 80.15 (2002): 2767-2769.

[4] Xie, Sishen, et al. "Mechanical and physical properties on carbon nanotube."*Journal of Physics and Chemistry of solids* 61.7 (2000): 1153-1158.

[5] Xie, Xiao-Lin, Yiu-Wing Mai, and Xing-Ping Zhou. "Dispersion and alignment of carbon nanotubes in polymer matrix: a review." *Materials Science and Engineering: R: Reports* 49.4 (2005): 89-112.

[6] Gojny, Florian H., et al. "Influence of different carbon nanotubes on the mechanical properties of epoxy matrix composites–a comparative study."*Composites Science and Technology* 65.15 (2005): 2300-2313.

[7] Sethi, Sanghamitra, Dinesh Kumar Rathore, and Bankim Chandra Ray. "Effects of temperature and loading speed on interface-dominated strength in fibre/polymer composites: An evaluation for in-situ environment." *Materials & Design* 65 (2015): 617-626.

[8] Ray, B. C. "Temperature effect during humid ageing on interfaces of glass and carbon fibers reinforced epoxy composites." *Journal of Colloid and Interface Science* 298.1 (2006): 111-117.

[9] Ray, Bankim Chandra, and Dinesh Rathore. "Durability and integrity studies of environmentally conditioned interfaces in fibrous polymeric composites: Critical concepts and comments." *Advances in colloid and interface science* 209 (2014): 68-83.

Chapter 2

Literature survey

2.1 Literature survey

Literature survey is documentation of comprehensive analysis of published/unpublished work from secondary bases information in the specific area of interest to researcher. One of the rich storage source for secondary information and researchers is used to spend their time to read several journals, newspapers and magazines. But now a days the computerized data base easily available and even accessible for literature search. Reviewing the literature helps to researcher to attention for further analysis more meaningful on specific aspects. So that the literature survey is the important for collecting secondary bases information for the area of research which might be helpful for research. The literature survey can be in field of area.

Some researchers have been attracted by the application of glass fibre /epoxy and carbon fibre/epoxy composite materials in low temperature and cryogenic environment [1][2]. Gong et al. [3] experimentally studied behaviour of the composite laminates at low temperature by 2 types of specimens 1) E-glass fibre and epoxy reinforced laminate. The volume fraction of fibre is 0.4 and 2) carbon fibre and epoxy reinforced laminate, volume fraction of fibre is 0.55 and made observations. Stress vs. strain curve shows linearity trend when sample exposed to low and room temperature conditions and the curve extends up to failure of the sample. At low temperatures brittleness is the failure characteristics found. The strength of the laminates at 77K have showing higher strength than the strength at 296K for each tested samples. At 77K the glass/epoxy and carbon/epoxy composites shows 15-20%, 30-40% than at 296K respectively. Hence here observed a significant enhancement in strength after cryogenic conditioning. At 296K the specimens have a less damaged area at the tip of the notch as compared with exposed at 77K. Because of micro rupture events might be damage area in composite. Some of the examples for micro ruptures like matrix – cracking, fibre/matrix interface split and delamination etc. Some of the energy is might be dissipated by each micro-rupture. Ray et al [4] used Araldite LY-556 as matrix and HY-951 as a hardener with silane treated woven fabric E-glass fibre to fabricate a laminated composite and evaluated its mechanical properties at low temperature

conditioning with different loading rates. The results reveled from the investigation the breaking load for untreated samples showed less strength than cryogenically treated samples for all loading rates. The reason might be when the sample expose to cryogenic temperatures the material experienced thermal shock along with matrix phase gets hardened. During conditioning polymer chains gets freeze leads to reduction in mobility of polymer. The scanning electron microscope image of fractured sample of glass/epoxy laminate at cryogenic conditioned shown in figure 2.1. The breaking load increases with increasing with cross head speed (mm/min) up to 50 mm/min, above the 50mm/min loading rate the breaking load decreases.

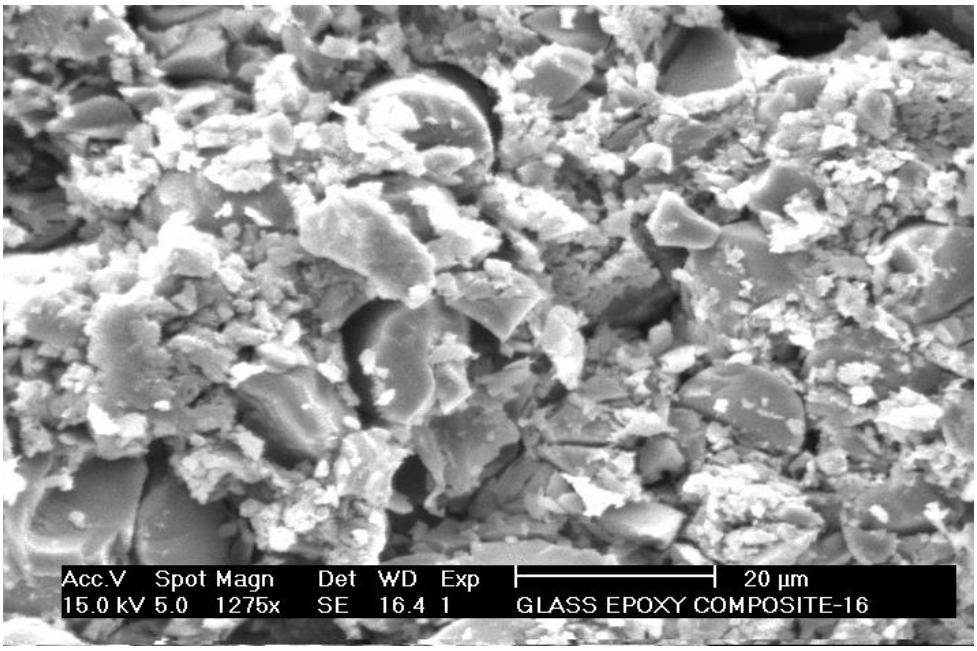

Figure 2.1: Schematic of Matrix cracking at cryogenic temperature i.e.77K. [4]

Sayer et al. [5] studied effect of the temperature on glass/carbon hybrid composite laminate under the impact loading. The results reveled from the investigation, hybrid laminate have high energy absorption compared to normal composite laminate at room temperature. Prasanth et al. [6] have been investigated on the Mode-I fracture analysis of thermally aged of glass/epoxy and glass-carbon/epoxy Hybrid Composites. There is a decrement in energy release rate of the glass epoxy aged specimen about 10%-15% of the same material. But in case of pristine condition and for glass/carbon hybrid specimens are showing decrement around 5%-10. The results carried out by specimens test DCB (Double Cantilever Beam conditioned at -20^{o}C for 500 hours. The results

shows that the decrement in energy release rate in glass/epoxy composite as compared to glass/carbon hybrid [6]. N.K Naik [7] et al studied on two different hybrid (glass/carbon) composites under quasi static loading. The results from the investigation revealed, for hybrid composites, the ultimate tensile strain and strength is higher whenever the glass fibres placing exterior and carbon fibre placing as compared to glass fibres placing interior and carbon fibres placing exterior. Chensong Dong [8] et al have been investigated on tensile strength and flexural strength of unidirectional hybrid composites. In laminated composites, the fibre phase plays a key role in mechanical properties on in-plane direction. These laminated composites are weak in z-direction (perpendicular to the plane of the laminate). The z-direction properties are generally limited by the matrix. Scientifically engineered nano-fillers have been reported to be more reliable choice to improve these properties, which have been acknowledged round the globe [9] [10]. Along with this improvement, it is of great interest to investigate the effect of nano filler incorporation on the environmental degradation of these potential materials. Qianqian Li et al [11] studied on mechanical properties and microstructure analysis of 0.03 wt. % single walled nanotubes (SWCNTs) as nano reinforcement, matrix as elastomeric epoxy with 0.3 wt. % block copolymer. The results showed there is increment in young's modulus, fracture stress and fracture strain of SWCNT-epoxy composite with block copolymer 141%, 127% and 43% respectively. Figure 2.2 represents stress vs. strain curves different composition of composites.

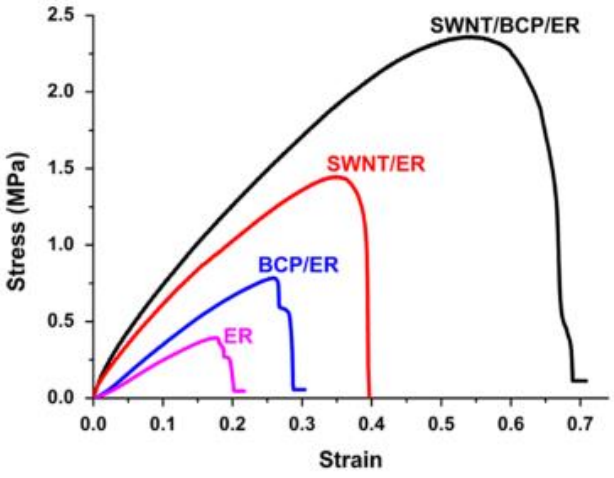

Figure 2.2: Tensile stress vs. strain curves of pure epoxy resin (ER), BCP-ER, SWCNT/ER, and SWCNT/BCP/ER

David Hui [12] et al studied on mechanical, thermal and electrical properties of aligned carbon nanotubes-polyimide composites. In the investigation they compared to properties of BPDA-PDA/CNT and pure poly amide. The results reveled from the investigation the strength and modulus of BPDA-PDA/CNT showed 2.3% and 12 times over the pure poly amide. Lu et al. [13] reported enhanced the glass transition temperature and the mechanical strength on addition of 0.25 wt. % of 3-glycidoxypropyltri-methoxysilane functionalized multi-walled carbon nanotubes prepared by electron beam (EB) irradiation. Further, few studies suggested the cryogenic property enhancement on adding CNTs to polymer resin. Figure 2.3 represents Vickers's hardness of pristine-MWCNT/epoxy and GPTMS-MWCNTS/epoxy.

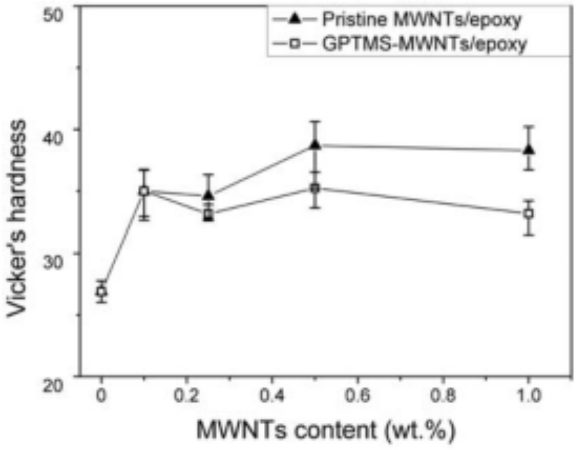

Figure 2.3: Vickers's hardness of pristine MWCNTs/epoxy and GPTMS-MWCNTs/epoxy

Chen et al. [14] studied on the cryogenic properties of CNT modified epoxy resin and noted improvement in tensile strength as compared to that of neat matrix. By addition of 2 wt. % CNT to epoxy the Young's modulus increased 17.2%, 20% for Room temperature and 77K respectively. The maximum strength showed 0.5wt. % CNT/epoxy as compared to other composites observed from the figure 2.4.

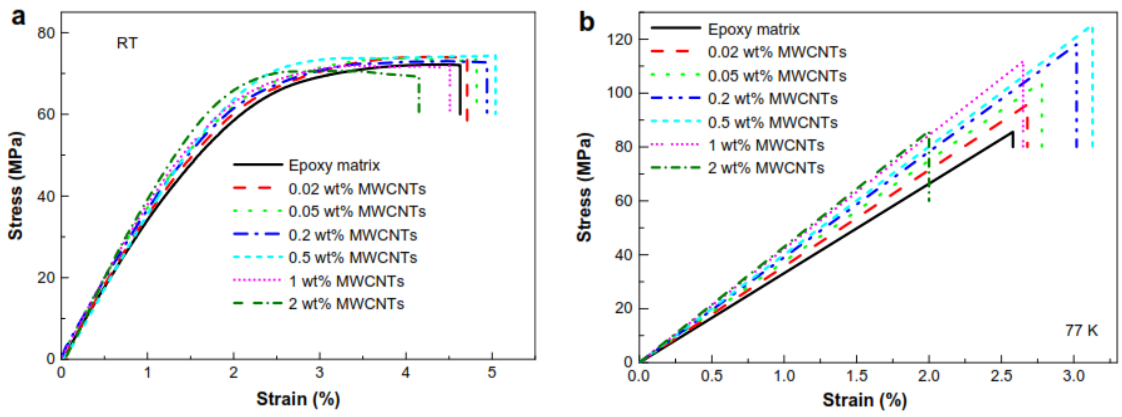

Figure 2.4: Stress vs. strain curves epoxy and MWCNTs/epoxy nano composites at (a) room temperature (b) 77K

Wei et al. [15] studied the flexural fatigue performance of CNT based polymer composites and found that as the temperature was reduced from room temperature to 77 K, there was increment in its fatigue resistance and fatigue performance was affected by the content of CNT used. Takeda et al. [16] investigated cryogenic mechanical properties of CNT modified woven glass/epoxy composites under tensile and fatigue loading. They observed that there was hardly any improvement in young's modulus and ultimate tensile strength on addition of CNT, but noticed improvement in fatigue resistance. Thus they demonstrated that addition of CNT has a potential to increase matrix dominated properties of composite materials at cryogenic temperatures.

References

[1] Kasen, M. B. "Cryogenic properties of filamentary-reinforced composites: an update." *Cryogenics* 21.6 (1981): 323-340.

[2] Hartwig, G., and S. Knaak. "Fibre-epoxy composites at low temperatures. "*Cryogenics* 24.11 (1984): 639-647.

[3] Gong, M., X. F. Wang, and J. H. Zhao. "Experimental study on mechanical behavior of laminates at low temperature." *Cryogenics* 47.1 (2007): 1-7.

[4] Kumar, Surendra, and B. C. Ray. "Mechanical behaviour of FRP composites at low temperature." (2007).

[5] Sayer, Metin, et al. "The effect of temperatures on hybrid composite laminates under impact loading." *Composites Part B: Engineering* 43.5 (2012): 2152-2160.

[6] Pandya, Kedar S., Ch Veerraju, and N. K. Naik. "Hybrid composites made of carbon and glass woven fabrics under quasi-static loading." *Materials & Design*32.7 (2011): 4094-4099.

[7] Dong, Chensong, and Ian J. Davies. "Flexural and tensile strengths of unidirectional hybrid epoxy composites reinforced by S-2 glass and T700S carbon fibres." *Materials & Design* 54 (2014): 955-966.

[8] Zhou, Yuanxin, et al. "Fabrication and characterization of carbon/epoxy composites mixed with multi-walled carbon nanotubes." *Materials Science and Engineering: A* 475.1 (2008): 157-165.

[9] Hwang, Gan Lin, Y-T. Shieh, and Kuo Chu Hwang. "Efficient Load Transfer to Polymer-Grafted Multiwalled Carbon Nanotubes in Polymer Composites."*Advanced Functional Materials* 14.5 (2004): 487-491.

[10] Li, Qianqian, et al. "Mechanical properties and microstructure of single-wall carbon nanotube/elastomeric epoxy composites with block copolymers."*Materials Letters* 125 (2014): 116-119.

[11] Jiang, Qian, et al. "Mechanical, electrical and thermal properties of aligned carbon nanotube/polyimide composites." *Composites Part B: Engineering* 56 (2014): 408-412.

[12] Lu, Yanyan, et al. "Mechanical properties of 3-glycidoxypropyltrimethoxysilane functionalized multi-walled carbon nanotubes/epoxy composites cured by electron beam irradiation." *Journal of Composite Materials* 47.14 (2013): 1685-1694.

[13] Chen, Zhen-Kun, et al. "Reinforcement of epoxy resins with multi-walled carbon nanotubes for enhancing cryogenic mechanical properties." *Polymer* 50.19 (2009): 4753-4759.

[14] Wei, Zhijuan, et al. "Flexural fatigue performance and electrical resistance response of carbon nanotube-based polymer composites at cryogenic temperatures." *Cryogenics* 59 (2014): 44-48.

[15] Takeda, Tomo, et al. "Cryogenic mechanical properties of woven glass/epoxy composites modified with multi-walled carbon nanotube and n-butyl glycidyl ether under tensile static and cyclic loadings." *Cryogenics* 58 (2013): 33-37.

Chapter 3

Experimental procedure

3.1 Materials

For fabricating a laminate used epoxy resin as matrix it is Diglycidyl ether of Bisphenol A (DGEBA) type epoxy. Triethylene tetra amine (TETA) used as hardener for curing. Both were purchased from Atul Industries Ltd, India. The diameter of μm 3K plain weave glass fiber was supplied by Saint Gobain, India. It served the need for reinforcement. Multi walled carbon tubes having an outer diameter of 6 to 9 nm and 5 μm length were supplied by Sigma-Aldrich. Some significant properties of the constituents of laminated composite are provided in Table-3.1.

Table 3.1: Properties of epoxy, glass fiber and MWCNTs

Properties	Epoxy	Glass fibre	MWCNTs
Density (g/cm^3)	1.16	2.58	0.037
Tensile strength (GPa)	0.12	3.42	11-63
Tensile modulus (GPa)	4.11	72.31	250-970

Specifications of glass woven fabric-
Warp and weft density: 16 and 14 yarns/inch,
Fabric weight: 360 gm.

3.2 Fabrication process

3.2.1 Dispersion of MWCNT into epoxy resin

Fabricate the MWCNT reinforced glass/epoxy (CNT/GE) composite, the epoxy resin was modified by incorporating MWCNTs in to it. The amount of CNT in CNT-GE composite was 0.3wt. % of epoxy for low temperature conditioning and 0.1 wt. %, 0.3 wt. % and 0.5 wt. % of epoxy for cryogenic treatment. Pre-calculated CNT was slowly poured into 150 mL of acetone. By using magnetic stirring the suspension was stirred at room temperature for 30 min at 1000 rpm. Followed by sonication for 30 min. Because of stirring and sonication, the CNTs gets distributed throughout suspension. After sonication the suspension was mixed with pre-calculated epoxy. Magnetic stirring of epoxy/CNT/acetone mixture was done at 1000 rpm for 1

hr at 70 °C. Sonication was again carried out at 70 °C upto evaporate entire acetone. During process might be air bubbles entrapped into the suspension. To remove these air bubbles, suspension was vacuum degassed for 18 hrs. The figure shows the dispersion of CNTs in composite and fabricate the fibre reinforced nanocomposite.

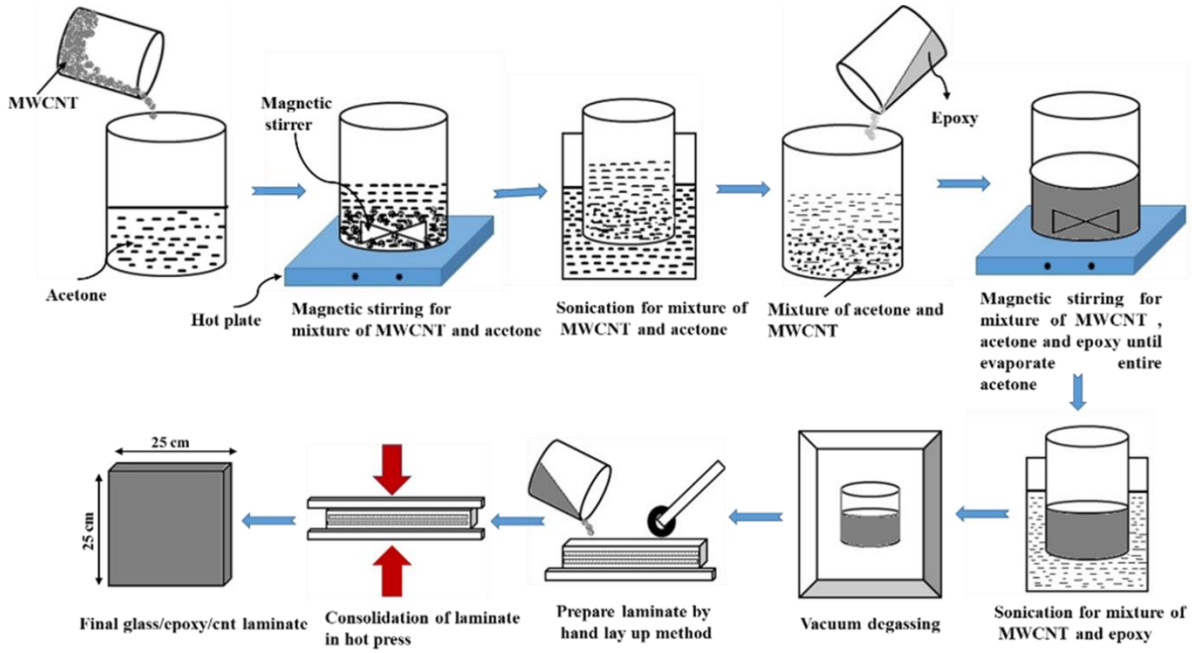

Fig 3.1: Dispersion of CNT in epoxy and further fabrication of laminated composite

3.2.2 Fabrication of Fiber reinforced nano-composites

After prepare the epoxy-CNT suspension mixed with required amount of hardener (10 wt. % of epoxy. The volume percentage of matrix and fibres 50 and 50 respectively. By using hand – layup method prepared the laminates. Followed by curing at 60°C and applied pressure 1 MPa in hot compressed press for 20 min. Likewise, using the same parameters for prepare CNT/GE as well as GE composites. For preparing GE composite, 14 layers glass fibre and required amount of epoxy and hardener. Laminate was cut for flexural test (as per ASTM D7264) by using diamond tipped cutter. The samples were then post-cured at 140 °C for 6 hr.

3.3 Material characterization

3.3.1 Mechanical characterization for low temperature conditioning

The samples were tested at different in-situ temperatures like -80 °C, -40 °C and RT (20 °C) maintain holding time 10 min. and 1 mm/min loading rate. The entire test carried out by using 3-point fixture environmental chamber of UTM-INSTRON 5967. Dynamical response of the sample carried out by using DMTA –E242.

3.3.2 Mechanical characterization for cryogenic conditioning

All prepared samples were dipped in liquid nitrogen (77K) for different time durations of 0 hr. (no conditioning), 0.25 hr., 1 hr., 4 hr. and 8 hr. After time duration samples drain out from the liquid nitrogen and testes instantaneously at RT. The flexural test carried out by using universal testing machine (UTM) –Instron 5967 as shown in figure 3.1. Here the sample dimensions as per ASTM D7264 and loading rate 1mm/min.

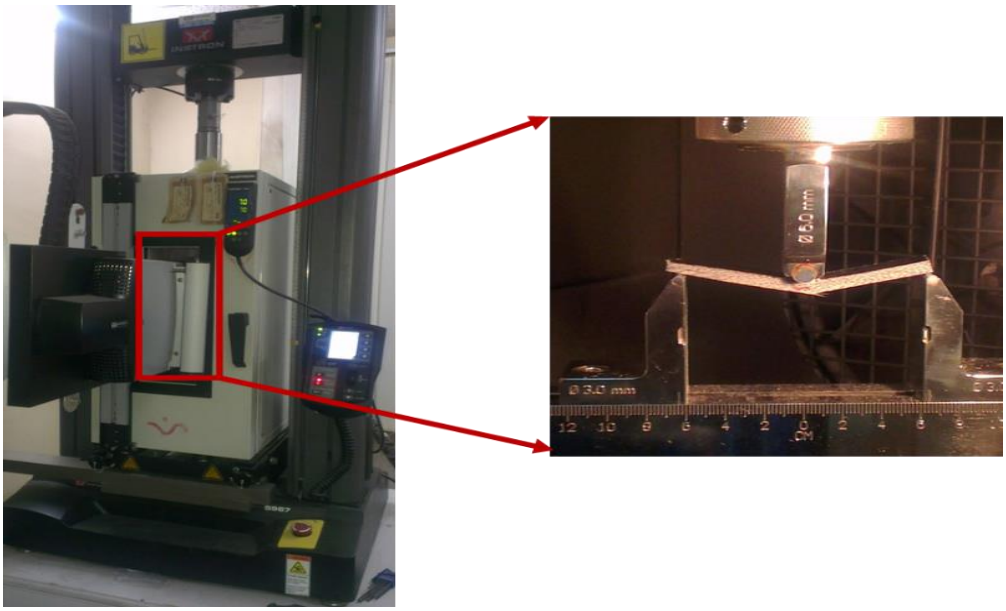

Figure 3.2: Experimental set up of UTM-Instron 5967

3.3.3 Dynamic mechanical Thermal Analyser (DMTA)

The temperature range of dynamic mechanical thermal analyzer is from -100°C to 200°C at 10°C heating rate. The samples were prepared by ASTM D7028. In DMTA, the specimens were loaded in a 3-point bending mode using a frequency of 10 Hz.

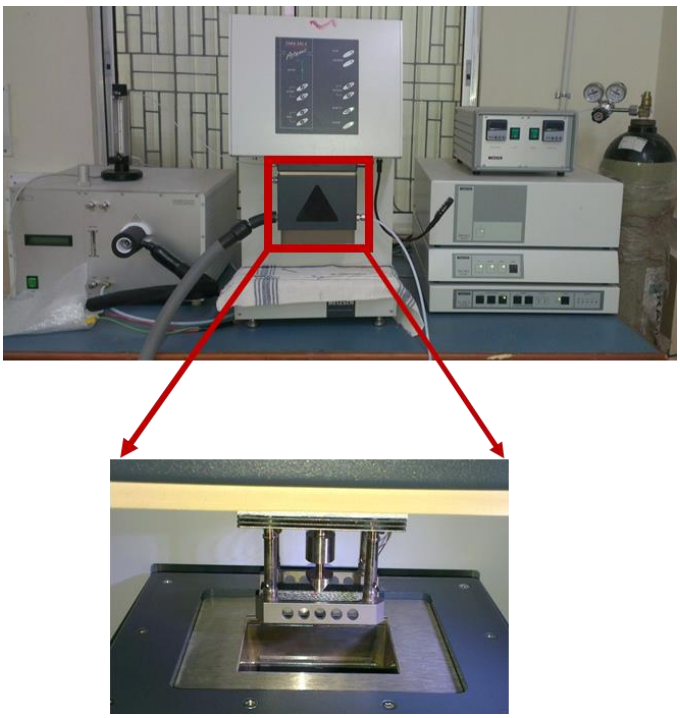

Figure 3.2 Experimental set up for dynamic mechanical thermal analyzer (DMTA)

3.3.4 Fractographic analysis

To analyses the failure modes of composites, their fracture surfaces were observed under Scanning Electron Microscope (SEM) with JEOL-JSM 6480 LVSEM operated at 20KV. The dispersion of MWCNTs in epoxy in case of CNT-GE composite is observed under Field Emission SEM. The surfaces of fractured samples were coated with a thin film of gold for increasing its electrical conductivity.

Chapter 4

Low temperature performance of CNT-GE composites

4.1 Introduction

FRP composites are most promising materials in the world because of their superior properties such as high strength to weight ratio, high corrosion resistance and low density etc. At low temperatures matrix plays key role in strengthening the composite [1] [2]. Modify the matrix by adding CNTs to get better mechanical and thermal properties at low temperatures [3] [4].

4.2 Results and discussion

4.2.1 Flexural behaviour at various testing temperatures

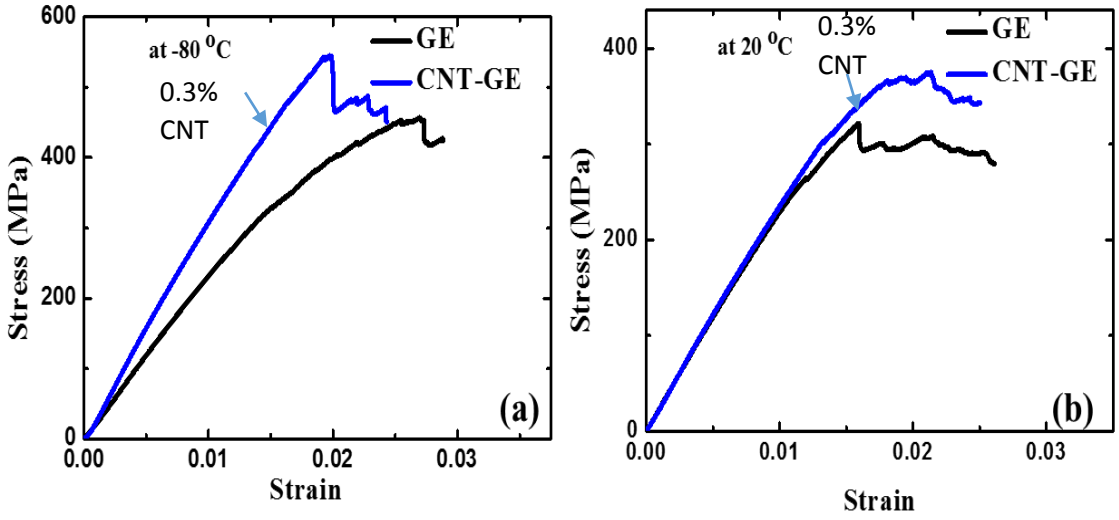

Figure 4.1: Flexural stress vs. strain curves for GE and CNT-GE composites for (a) -80^{0}C (b) 20^{0}C

The above figure 4.1 represents the stress vs. strain curves of CNT/Glass epoxy and glass epoxy at low (-80^{0}C) and RT (20^{0}C). Figure 4 represents the flexural strength and flexural modulus vs. temperature for CNT/glass epoxy and glass epoxy (GE).

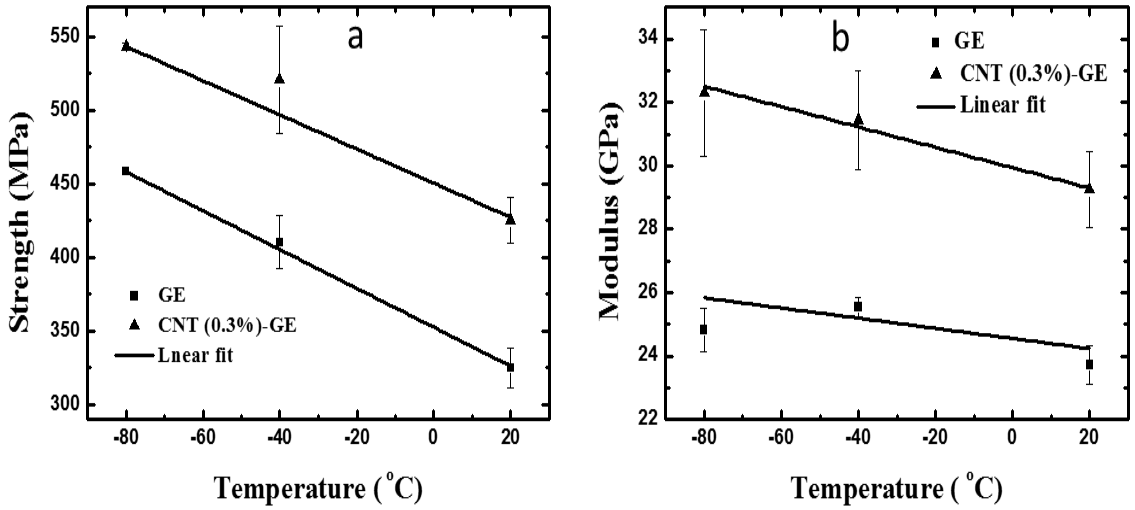

Figure 4.2: Variation in (a) Flexural strength (b) Flexural modulus with testing temperatures for GE and CNT-GE

From the figure 4.2 that the flexural modulus and strength both are dependent on temperature for CNT/GE and GE. The below equations explains that strength and modulus dependency of CNT/GE and GE on temperatures (for low temperatures (-80 °C, -40 °C and RT). For GE composites:

For Glass/epoxy composites:

$$E\ (GPa) = 24.53 - 0.03\ T\ (°C) \quad (1)$$

$$\sigma\ (MPa) = 370.56 - 1.1\ T(°C) \quad (2)$$

For CNT/GE composites:

$$E\ (GPa) = 28.84 - 0.05\ T\ (°C) \quad (3)$$

$$\sigma\ (MPa) = 435.45 - 1.36\ T(°C) \quad (4)$$

The rate of decrement in modulus with increase in the temperature observed from the equations (1) and (3). The decrement rate is 0.03 GPa/°C and 0.05GPa/°C for controlled GE and CNT/GE respectively. From the equations (2) and (4) the rate of decrement in strength 1.1 MPa/°C and 1.36 MPa/°C for controlled GE and CNT/GE. The CNT/GE composite shows the higher strength than glass/epoxy composite at room temperature (RT). Because CNT have high interfacial area in CNT-epoxy matrix, the load transfer ability increases across the interface. At low

temperatures the strength and modulus improves than at room temperature. It might be attributed by two reasons: (a) Hardening of matrix and (b) interfacial locking. Because of matrix hardening the polymer molecules have less mobility results rigidity of matrix. Interfacial interlocking, as temperature is decreasing, mechanical gripping established between CNT and epoxy due to differential in thermal coefficients. The above two factors mainly effecting the strength and modulus in case low temperature conditioning.

4.2.2 Dynamic Mechanical Thermal Analysis (DMTA)

Dynamical mechanical thermal analysis is devise to find the visco elastic response of the any material. In this device applies a force (load) dynamically with wide range of temperature. Visco elastic means the material show viscous property as well as elastic property. The storage/elastic modulus (E′) obtained from DMTA. The term (E') represents the elastic property of the material. Whereas the loss/viscous modulus (E″) reflects the viscous property of material. The loss factor denoted as tanδ. The damping tendency of the material. Damping means dissipating energy under cyclic loads. It defined that ratio of E″ to E′. The E′, E″ and tanδ are determined using the following equations [5] [6].

$$E^{'} = \frac{\sigma_1}{\varepsilon_1}\cos\delta \tag{5}$$

$$E^{''} = \frac{\sigma_1}{\varepsilon_1}\sin\delta \tag{6}$$

$$\tan\delta = \frac{E^{''}}{E^{'}} \tag{7}$$

Where, σ_1 and ε_1 represent the stress at peak and strain at peak respectively and δ is the phase difference between the dynamic stress to dynamic strain.

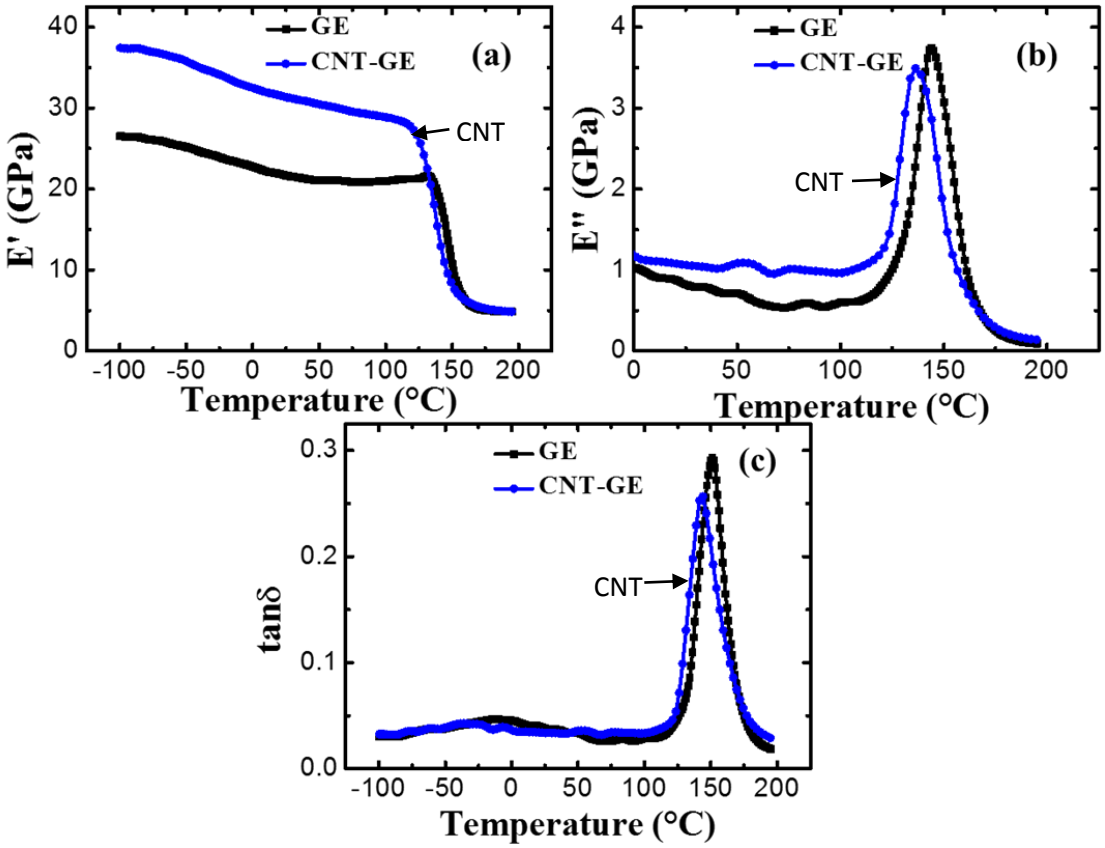

Figure 4.3: Variation in (a) E′, (b) E″ and (c) tanδ with temperature for GE and CNT-GE composites.

Figure 4.3 refers variation in storage modulus (E′), loss modulus (E″) and tanδ with temperature for GE and CNT/GE composites. The reduction rate of E′ with temperature (upto T_g) is more in CNT/GE composite compare to GE composite. The glass transition temperature (T_g) of the material represents the change in slope of storage modulus and temperature curve. From figure 3.3 (a) it can be observed because of addition of 0.3 wt. % CNTs lowering in T_g from 136 °C to 125 °C. Due to entrapped CNTs into polymeric chains it results to reduce the formation of cross links. Figure 4.3 (b) represents the variation in loss modulus (E″) because of incorporation of CNTs in composite. Figure 4.3 (c) show the tanδ value, it gives the damping property of the material.

4.2.3 Constitutive flexural deformation model

In general, deformation/failure of the laminated composite is the final result of number of failure micro mechanisms such as formation of local flexure, micro buckling, etc. The results in failure modes like matrix cracking, fiber/matrix interfacial debonding. By using Weibull distribution function, stress (σ)-strain (ε) relationship for a fiber reinforced composite can be modelled by the given equations

$$\sigma = E\varepsilon \exp\left[-\left(\frac{E\varepsilon}{\sigma_o}\right)^{\beta}\right] \tag{8}$$

Where E represents flexural modulus of the composite. Weibull scale (σ_o) and shape parameter (β) respectively. The nominal strength of composite is denoted byσ_o, randomness in strength was measured by β. By taking double logarithm both sides of the equation 8 to evaluate σ_o and β

$$\ln\left[\ln\left(\frac{E\varepsilon}{\sigma}\right)\right] = \beta\ \ln(E\varepsilon) - \beta \ln(\sigma_o) \tag{9}$$

Equation 9 represents a straight line between $\ln(E\varepsilon)$ and $\ln\left[\ln\left(\frac{E\varepsilon}{\sigma}\right)\right]$ which can be seen from figure 4.4. The slope of the straight line gives the value of β and from the value of intercept and β the value of σ_o can be determined.

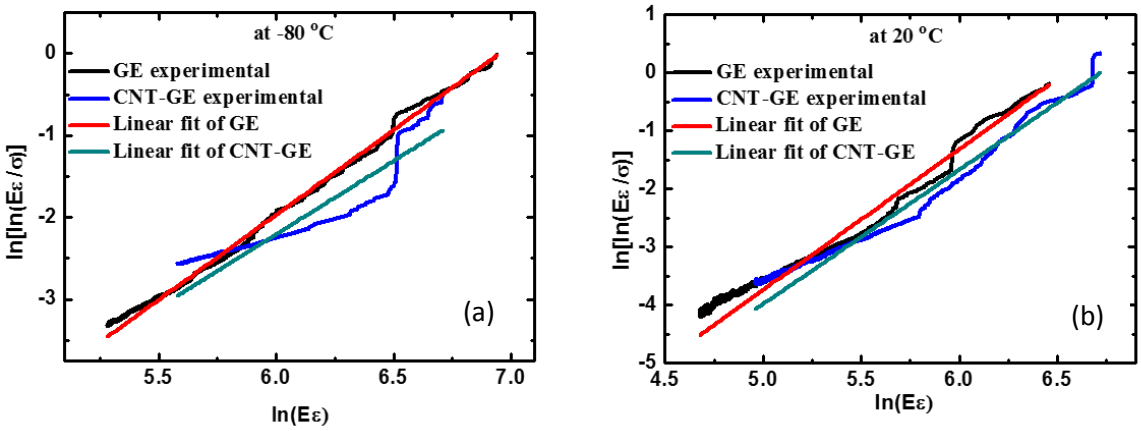

Figure 4.4: Weibull fitting of experimental for GE and CNT-GE at (a) -80° C and (b) 20° C

The parameters of the Weibull function for GE and CNT-GE composites obtained from figure 4.4 at various testing temperatures are reported in table 4.1

Table 4.1

Weibull scale (σ_o) and shape (β) parameters for GE and CNT-GE composites at various temperatures

Temperature (°C)	**Weibull scale parameter σ_o (MPa)**		**Weibull shape parameter (β)**	
	GE	**CNT-GE**	**GE**	**CNT-GE**
-80	1051.6±5.3	1572.5±292.6	2.01±0.13	1.73±0.23
-40	852.4±45.3	1170.3±228.7	2.18±0.08	2.43±0.18
20	757.6±21.7	818.2±33.8	2.38±0.06	2.39±0.12

For both GE and CNT-GE composites, σ_o follows a similar trend that of similar to flexural strength observed in figure. Alters the value of β by addition of CNT content to GE. Find the σ_o and β values by using equation 9 and listed the values in table 3.1. The stress-strain curve was drawn for GE and CNT-GE composites at -80 °C,-40°C and 20°C. Superimposed with the experimental data as shown in figure 4.5. From figure 4.5 it can be evident that the experimental and simulated stress vs. strain curves shows same kind of trend.

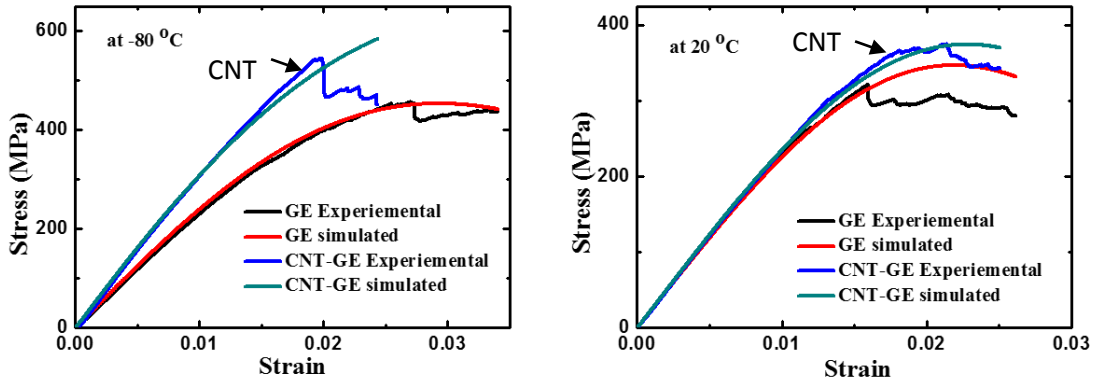

Figure 4.5: Comparison between experimental and simulated stress vs. strain for GE and CNT-GE composites at (a) -80°C and (b) room temperature (20°C)

4.2.4 Fractography

The failure analysis of the GE and CNT (0.3%) -GE composites was carried out by using scanning electron microscope (SEM). Fractured surfaces of GE composites at various testing temperatures of SEM images observed from figure. Exposure to low temperature (-80 °C), due to immobility of polymer molecules results the rigid of composite. Ultimately the material loss its ductility and toughness. From figure3.6 (a) it can be observed that, at low temperatures the dominating failure mode is brittle rupture of the matrix for GE composites. At low temperature, the figure3.6 (b) indicates fractured surface in conjunction with debris and loose materials. Because of shear loading the formation of debris failure modes attributed. The fractured surfaces figure 3.6 (b) indicate fiber imprints and river line markings on the polymer in the inter-filamentary region.

The major failure modes like fibre/matrix debonding observed at room temperature. At room temperature from figure c. The fibre fragments and river line marking failure modes occur due to low temperature conditions. From figure d it can be observed that scarp. These scarps type failure mode observed at the end of the fibre due to applying load matrix gets deforms.

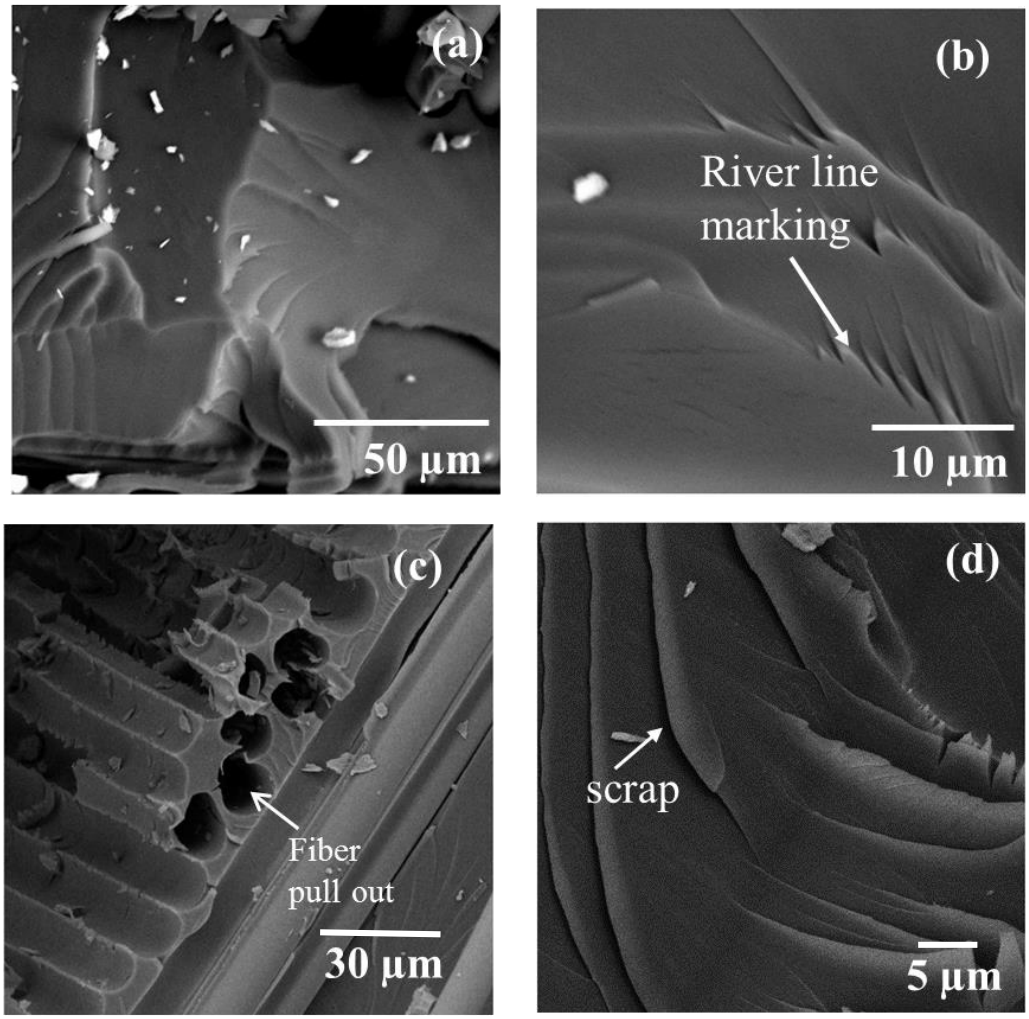

Figure 4.6: SEM images of fractured surfaces of GE composites of after flexural testing at (a, b) -80°C and (c, d) room temperature (20°C)

The ribs was formed in case of CNT (0.3%)-GE composites, tested at low temperature (-80 °C), was noticed as shown in figure 4.7(a). These ribs are formed might be high interlaminar matrix thickness. In case of bulk polymer materials the ribs are arrest the cracks. Hence, it suggests ribs may hold the enhancement in strength in case of CNT-GE composite. Figure 3.6 c represents the delamination and fibre pull out failure modes in CNT/GE at room temperature. Figure 4.7 (b) indicates the river line markings on the matrix surface, which is a signature of the brittle failure. From figure 4.7(d) it can be observed formation of scarps on the matrix, at the end to fibers. Further observed under applied load, mirror, mist and hackle zones are present at the cross section of fibre shown in figure 4.7 (c).

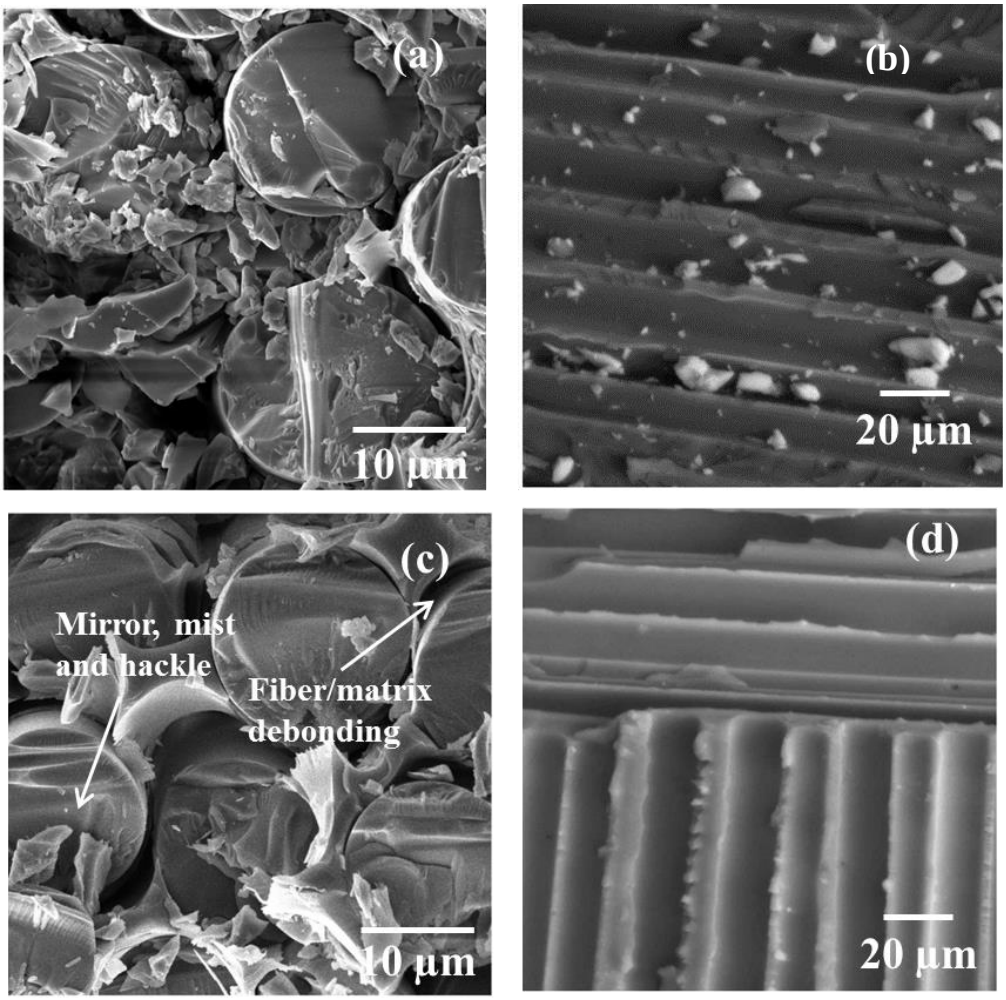

Figure 4.7: SEM images of the fractured surfaces of CNT – GE composites for after flexural testing at (a, b) -80^{0}C and (c, d) room temperature (20^{0}C)

Figure 4.8 (a) represents the fractured CNT-GE composite at room temperature showing uniform distribution and dispersion of the CNTs in polymeric matrix. The good dispersion of CNTs give the better mechanical properties to composite. At room temperature the CNT-GE composite shoes good interfacial bonding between CNT and epoxy. Figure 4.8 (b) shows the CNT pull out phenomena, reported by various researchers which enhances the damage tolerance of the composite.

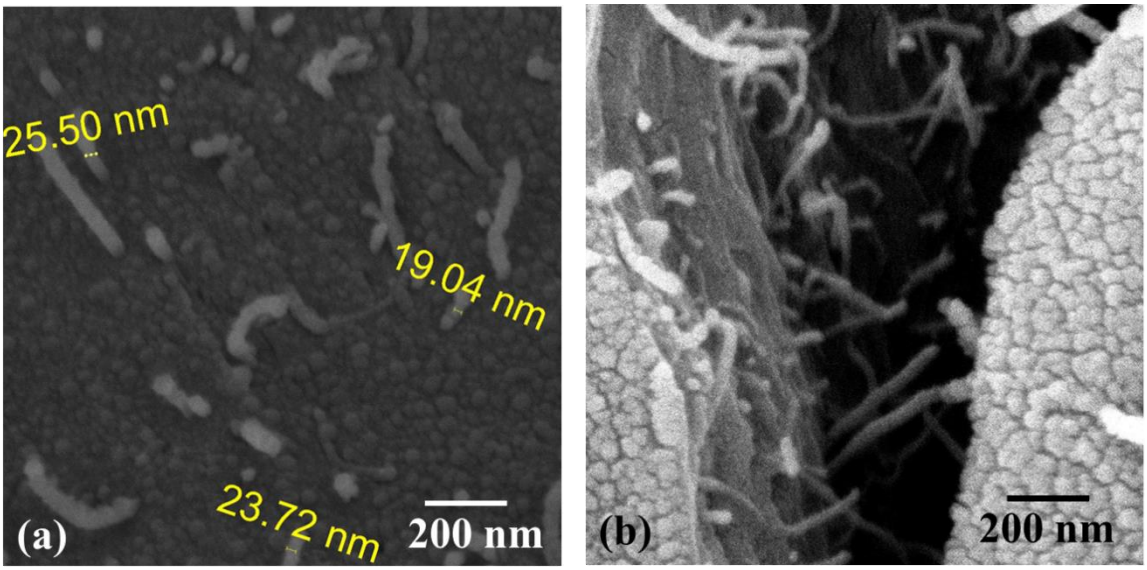

Figure 4.8: SEM images of the fractured surfaces of CNT-GE composite after flexural testing at room temperature (20^0C) showing (a) distribution of MWCNTs in the epoxy (b) crack bridging by MWCNTs.

4.3 Conclusion

The effect of in-service temperature on mechanical behaviour of CNT-GE and GE composites was evaluated. At low in-service temperature environment, the CNT-GE composites exhibited higher elastic modulus compared to GE composites, as confirmed from DMTA within the studied range of temperature. Furthermore, addition of 0.3 wt. % MWCNT into GE composite significantly lowered the T_g by 12 °C due to hindrance in crosslink formations. The reinforcement efficiency (relative change in modulus) due to CNT incorporation in GE composite is as high as 30%, when the testing temperature was -80 °C. It further reduces to 23% when tested at room temperature (20 °C). The rate of degradation is significantly higher for CNT-GE composites than GE composites (reducing the modulus of CNT-GE composite by 50% than that of GE composite) due to presence of high interfacial area, providing more damage nucleation sites, causing remarkable interfacial debonding. Within the temperature range of -80 °C to 20 °C, the magnitude of Weibull scale parameter (σ_o) was found to be enhanced by incorporation of 0.3 wt. % MWCNT in GE composite. At -80 °C, the relative increment in σ_o for CNT-GE composite was 50% with respect to controlled GE composite. The dependency of

in-service temperature on mechanical properties is more pivotal in case of MWCNT modified GE composites than conventional GE composites.

References

[1] Lin, Y-S., C-H. Hu, and C-A. Hsiao. "Enhanced scratch resistance of flexible carbon fiber-reinforced polymer composites by low temperature plasma-polymerized organosilicon oxynitride: The effects of nitrogen addition."*Composites Science and Technology* 71.13 (2011): 1579-1586.

[2] Sethi, Sanghamitra, and Bankim Chandra Ray. "An assessment of mechanical behavior and fractography study of glass/epoxy composites at different temperatures and loading speeds." *Materials & Design* 64 (2014): 160-165.

[3] Jäckel, M. "Thermal properties of polymer/particle composites at low temperatures." *Cryogenics* 35.11 (1995): 713-716.

[4] Dutta, Piyush K., and David Hui. "Low-temperature and freeze-thaw durability of thick composites." *Composites Part B: Engineering* 27.3 (1996): 371-379.

[5] Guadagno, L., et al. "Effect of functionalization on the thermo-mechanical and electrical behavior of multi-wall carbon nanotube/epoxy composites." *Carbon*49.6 (2011): 1919-1930.

[6] Prolongo, S. G., M. R. Gude, and A. Ureña. "Improving the flexural and thermomechanical properties of amino-functionalized carbon nanotube/epoxy composites by using a pre-curing treatment." *Composites Science and Technology* 71.5 (2011): 765-771.

Chapter 5

Cryogenic temperature performance of CNT-GE composite

5.1 Introduction

FRP composites find application in aerospace industry, marine vehicles, structural applications, cryogenic fuel tanks, hydrogen storage tanks, pressure vessels, thermal insulators, etc.[1][2] FRP composites have been proved to be a better choice of material in replacing metallic materials in various cryogenic applications mostly cryogenic fuel tanks for its efficient storage and transportation [3][4]. This is due to their desirable properties like high resistance to corrosion, high specific strength, specific stiffness, etc. Modifying the matrix using nano-fillers is a recent trend observed in fabrication of FRP composites to enhance the matrix dominated properties [5] [6] [7].

5.2 Results and discussion

5.2.1 Flexural performance after cryogenic treatment

The Figure 5.1 shows flexural stress vs. strain curves for GE and CNT-GE (all the compositions) samples conditioned in liquid nitrogen for 0 hr, 0.25 hr, 1 hr and 4 hr. Figure 5.2 and 5.3 represents the flexural properties i.e. flexural modulus and flexural strength plotted against conditioning time for various amount CNT content. From Figure 5.2 the flexural strength of CNT (0.1%)-GE shows maximum strength as fabricated conditioned. The increment in strength of CNT (0.1%)-GE around 32.7% than other CNT-GE and GE composites.

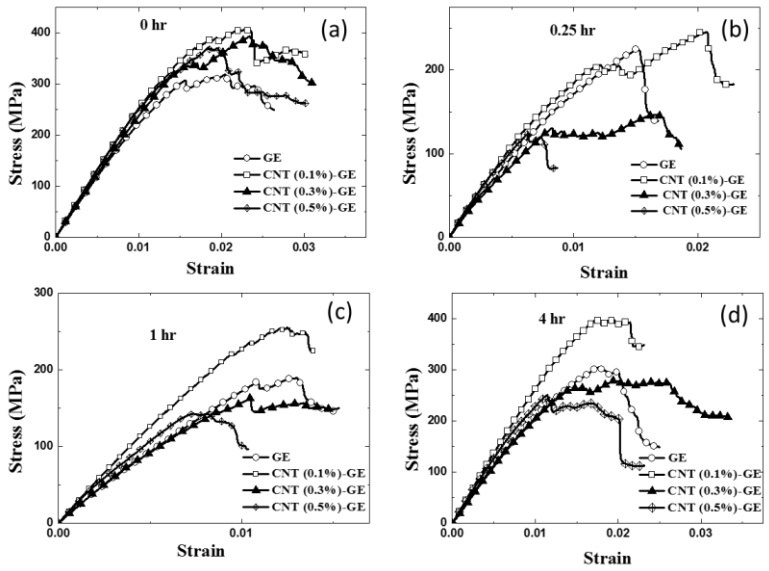

Figure 5.1: Flexural stress vs .strain curves for GE and CNT-GE composites conditioned in liquid nitrogen for (a) 0hr (b) 0.25 hr (c) 1 hr and (d) 4hr.

This may be due to increased CNT/epoxy interfacial area due to high surface area of CNTs and hence more stress/load transfer across the interface takes place.

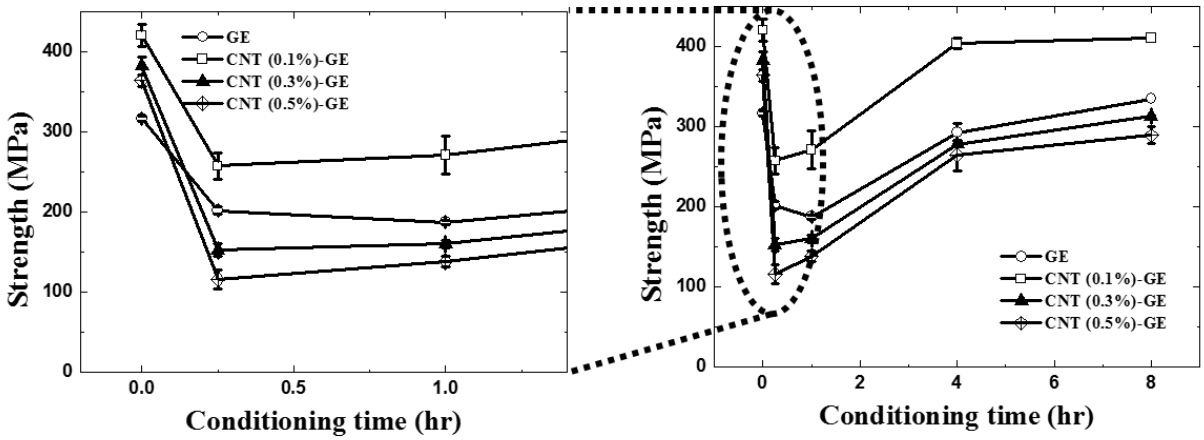

Figure 5.2: flexural strength for GE and CNT-GE composites with conditioning time in liquid nitrogen.

Hence, it results in more stress required to break the sample. At room temperature the strength of CNT (0.3%)-GE and CNT (0.5%)-GE decreases compared to CNT (0.1%)-GE due to

agglomeration CNTs. Due to agglomerated CNTs will not able to show their nano scale properties. It results their interfacial area decreases. Hence this lead to decrement in strength. The flexural modulus also follow the same trend that of flexural strength for all composites observed from figure.

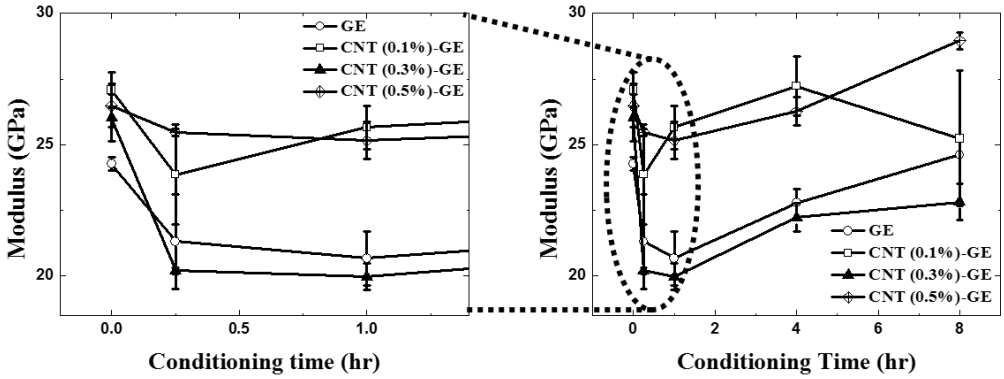

Figure 5.3 Variation in flexural modulus for GE and CNT-GE composites with conditioning time in liquid nitrogen.

From figure 5.3 it can be seen that after 0.25 hr conditioning, there is drop in modulus for all the composites as compared to the modulus obtained for samples with no conditioning. It is following the same fashion followed by variation in strength found after 0.25 hr conditioning. After 1 hr conditioning, the modulus of all the composites except CNT (0.1%)-GE composite decreased further.

0.25 hr thermal shock conditioning makes the polymeric chains gets frozen and results in drastic matrix embrittlement. From figure 5.3 it can be observed that enhancement in mechanical properties by the addition of CNTs into GE composites. The samples expose for 0.25 hr in liquid nitrogen (-196°C), the strength and modulus drastically decreased. Whenever samples brought from -196 ^{o}C to room temperature the samples experienced thermal shock. In case of GE composites, due to differential in thermal contractions between glass fibre and epoxy may have generate localized thermal stress at interface of epoxy and fibre. Due to this thermal stresses leads to formation of micro-cracks and micro voids at the interface. Interfacial debonding is more in case of CNT-GE composite. Because in CNT-GE composite exist another interface that is CNT/epoxy. Also, differential thermal contraction is more in case of epoxy (6.2×10^{-5} K^{-1}) than CNT ($0.73–1.49 \times 10^{-5}$ K^{-1}). The drop in strength by 36.2 %, 38.7 %, 60.2 % and 68.1 %

in case of GE composite, CNT (0.1%)-GE composite, CNT (0.3%)-GE composite and CNT (0.5 %)-GE composite respectively after 0.25 hr conditioning in liquid nitrogen. Further, exposed the samples for 1 hr and test instantaneously. Because of formation of micro cracks, micro voids and insufficient matrix hardening the strength and the modulus of the GE composite decreases as compared to all CNT-GE composites. The CNT-GE (all the compositions) composite showed relative increment in strength and modulus as compared to obtained after 0.25 hr conditioning. This might be CNTs have obstruct the path propagation of cracks. Further exposing the samples for 4 hr, recovery in flexural strength and modulus was observed for the GE composite and CNT-GE composites (all compositions). Because of high amount of matrix gets hardening due to available of enough time to polymer chains to freeze. Also, because of gripping between CNT/epoxy improves the stiffness of the composite. The increment in strength by 45.2%, 55.82%, 73.9% and 126% of GE, CNT (0.1%)-GE, CNT (0.3%)-GE and CNT (0.5%)-GE respectively as compared to flexural strength of 0.25hr conditioning. A very little increment in strength observed after exposed samples for 8hrs compared to expose for 4hrs. This may attributed the density of micro-cracks remained same and hence not much significant increase in strength was observed.

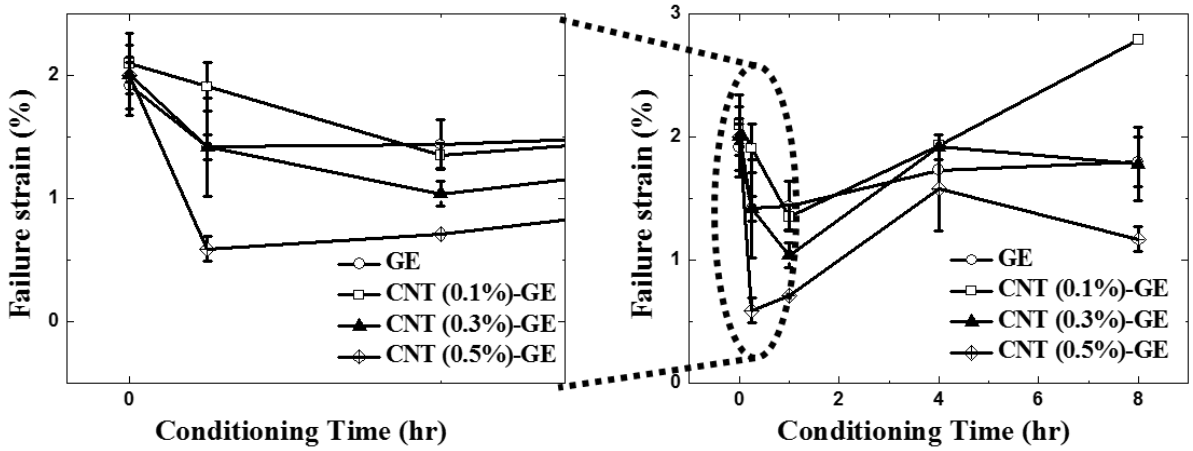

Figure 5.4: Variation in failure strain for GE and CNT-GE composites with liquid conditioning time.

From figure 5.4 it can be observed that the strain to failure is more in case of CNT (0.1%)-GE than other all composites .It represents the toughness of the material. For short time (0.25hr.)

conditioning ductility is reduced due to thermal shock resulting frozen polymer chains. For long term (4hr.) conditioning the residual stresses ahead of crack tip is released resulting enhancement in ductility and toughness.

From the above discussion, that the mechanical properties of GE and CNT modified GE composite is strongly impact on the duration of liquid nitrogen conditioning and content of CNT. Structural integrity of GE composite could be efficiently improved with better reliable by addition of CNT (0.1%).

5.2.2 Damage constitutive failure model

For durable and safe applications to it is need to design the critical parameters properly .With the help of Weibull probability of functions modelling of stress strain relationship. The simulated stress can be obtained with the help of equations from chapter 4.

Figure 5.5 represents the Weibull fitting plots of GE and CNT (0.1%) samples conditioned for 0 hr, 0.25 hr, 1 hr and 4 hr and the calculated Weibull scale parameter(β)and nominal strength (σ_o) values are plotted in figure 4.6 . From the Figure 4.6, it can be observed that the value of nominal strength (σ_o) reduces after conditioning GE and CNT-GE (all compositions) composites after exposed to liquid nitrogen for 0.25 hr and further increases (except GE composite) as the conditioning time increases to 1 hr. From the figure the trend in nominal strength (σ_o) is quite similar to that of trend obtained for flexural strength. After short term conditioning, the value of Weibull scale parameter (β) was showed maximum for CNT (0.1%)-GE composite showing minimum scatter. Further exposure of 1 hr and 4 hr resulted in decreased variation in β. Overall results showed that the strength of all these composites obey the Weibull distribution model.

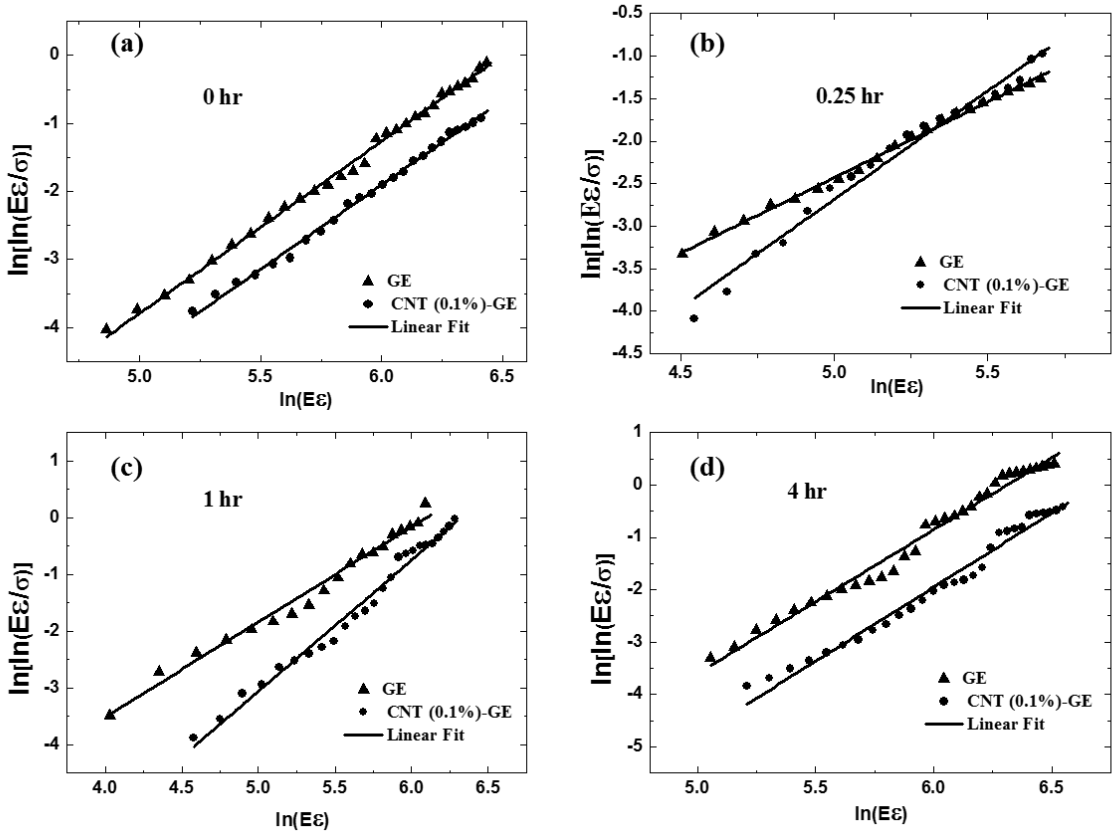

Figure 5.5: Weibull fitting for experimental GE and CNT (0.1%)-GE composite conditioned in liquid nitrogen (a) 0hr (b)0.25hr (c) 1 hr and (d) 4hr

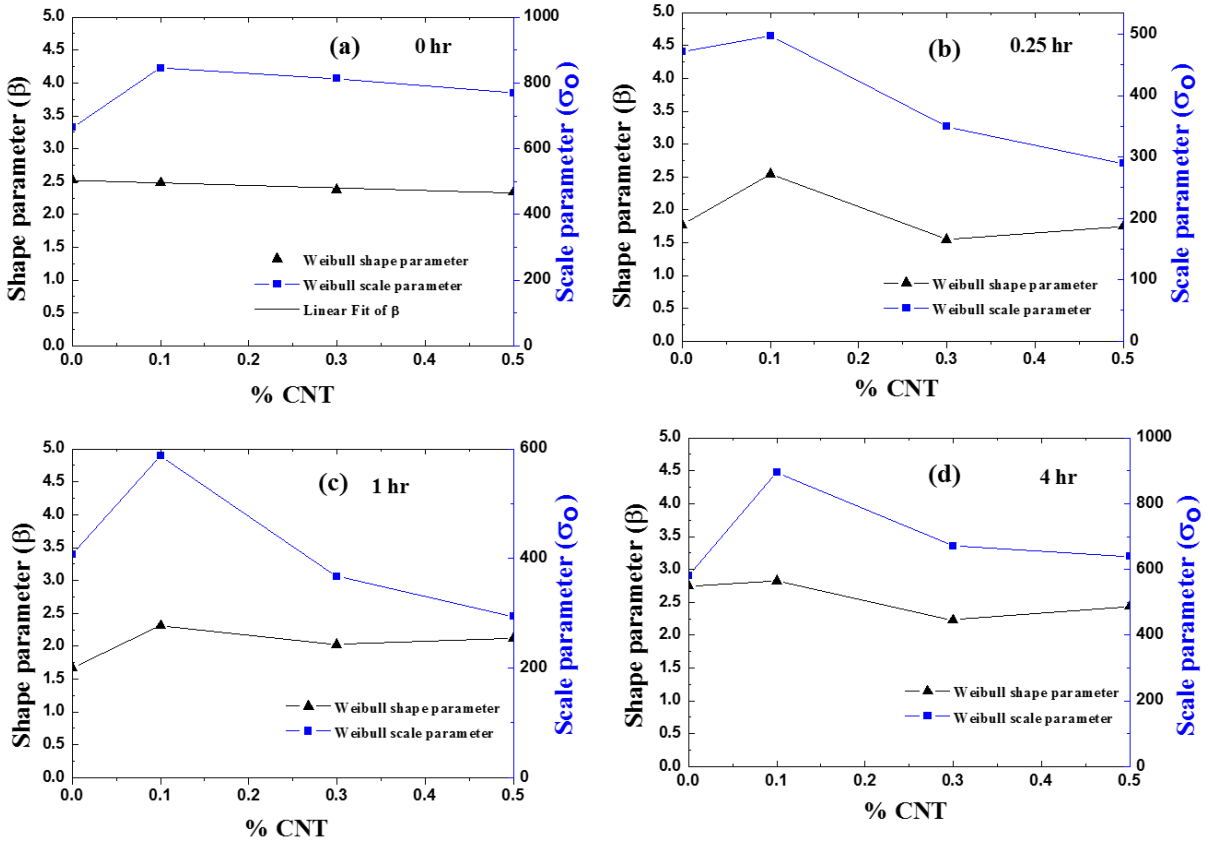

Figure 5.6: Variation in Weibull shape parameter and scale parameter with varying of CNT content and conditioning time.

The figure 5.7 represents the experimental and simulated stress vs. strain curves for different conditioning time of 0 hr, 0.25 hr, 1 hr and 4 hr for different compositions. This shows that the experimental stress vs. strain curves are in very close with the simulated stress vs. strain curves for 0, 1hr and 4hrs whereas in case of short term exposure (0.25 hr) the experimental and simulated stress-strain curves are not matching to that extent. Hence this implies that the materials mechanical response become less uniform and less predictable under short term liquid nitrogen exposure or thermal shock.

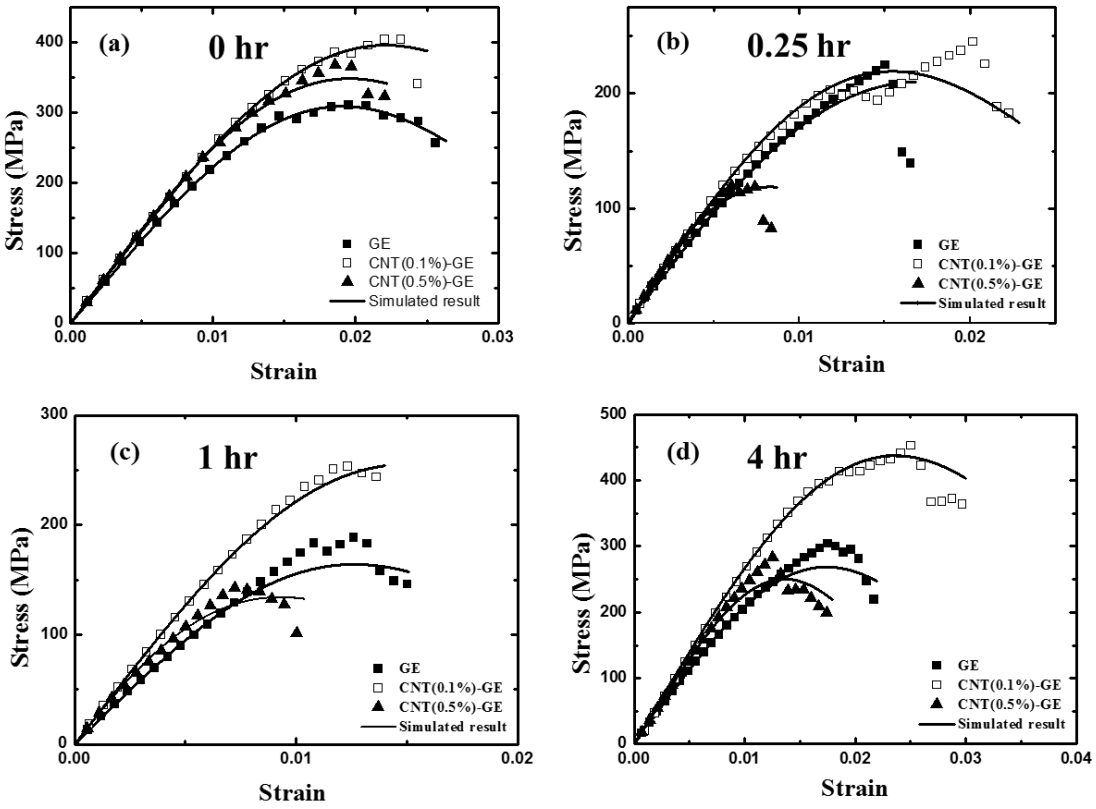

Figure 5**.7:** comparison between experimental and simulated flexural stress vs. strain curves for GE and CNT-GE composites.

5.3 Fractography

Scanning Electron Microscopy (SEM) technique was adopted to identify the failure mechanisms responsible for the overall failure of the GE and the CNT-GE composites. Figure 5.8 shows the SEM images of fractured surfaces of GE composite and CNT (0.1%, 0.3%, 0.5%)-GE composite after conditioning them in liquid nitrogen for 0.25 hr. It is evident from Figure 5.8 (a) that in case of GE composite, the major failure modes are matrix cracking, due to differential thermal contractions and formation of ribs.

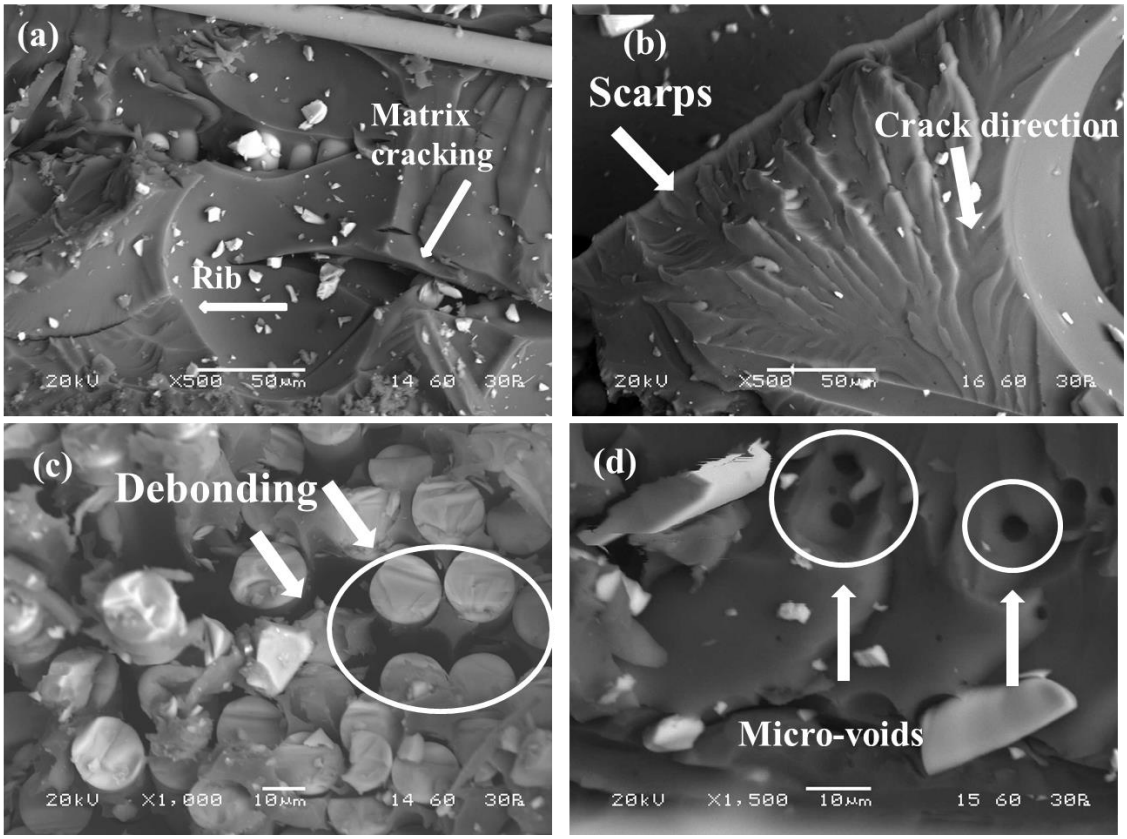

Figure 5.8 SEM micrographs of the samples of (a) GE, (b) CNT (0.1%)-GE, (c) CNT (0.3%)-GE and (d) CNT (0.5%)-GE composites conditioned in liquid nitrogen for 0.25 hr.

Figure 5.8 (b) shows the fractograph for CNT (0.1%)-GE composite and indicates that generation of scarps due to multiple micro-cracks lowers the strength of this composite. in Figure 5.8 (c). Debonding results due to large interfacial shear stress generated between fiber and matrix at the time of loading. These micro-cracks are generated due to coalesce of many micro-voids formed in the matrix. This can be seen from Figure 5.8 (d) of CNT (0.5%)-GE composite.

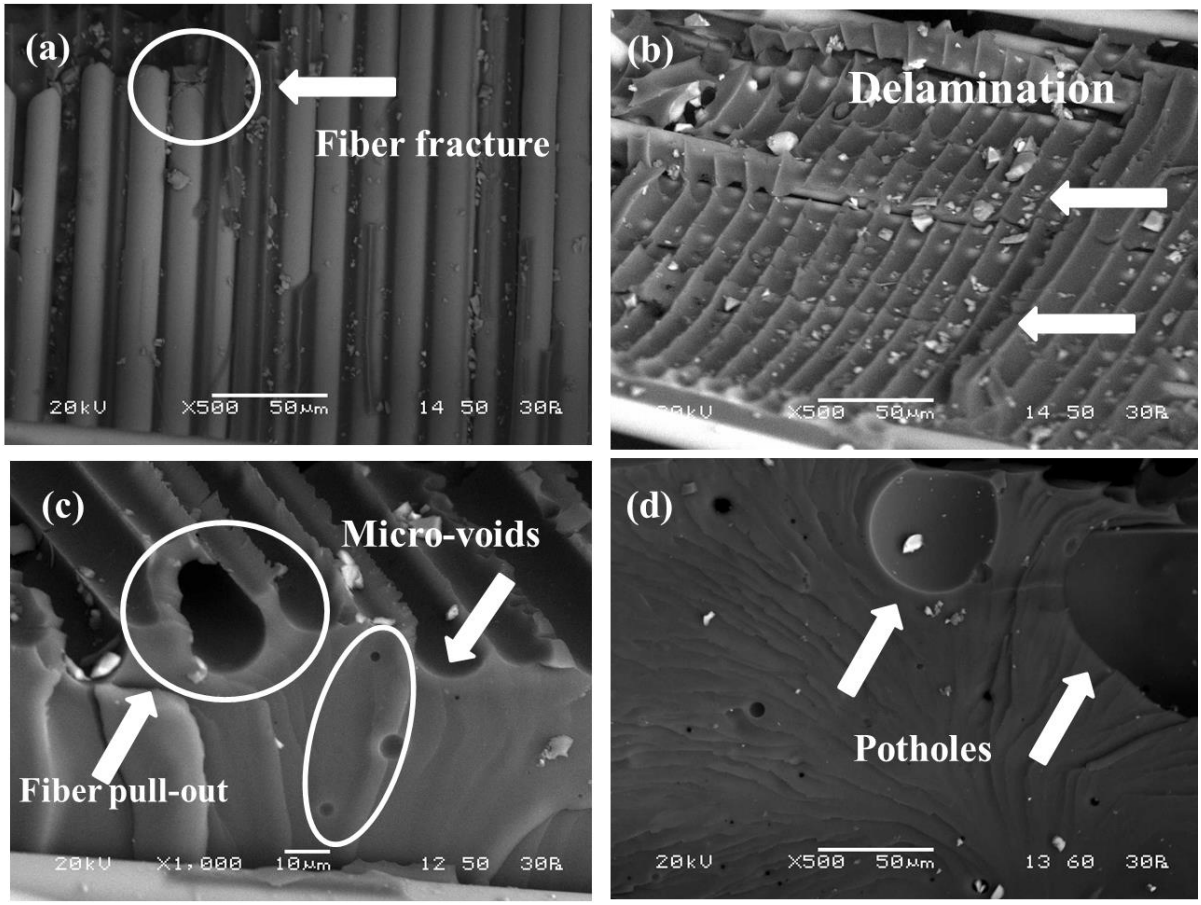

Figure 5.9: SEM micrographs of fractured samples of (a) GE, (b) CNT (0.1%)-GE, (c) CNT (0.3%)-GE and (d) CNT (0.5%)-GE composites conditioned in liquid nitrogen for 4 hr.

Fibre fracture is the mechanism accountable for failure of GE composite after 4 hr. Also, as fiber fracture is more energy absorbing failure mode, it can be observed from figure 5.9(a). Debries are formed as shown in Figure 5.9 (b) due to abrasion between hardened matrix and fiber. The fracture will proceed and the broken fibers will ultimately be pulled out of the matrix as shown in Figure 5.9 (c). Extensive river line markings and potholes, in addition to voids are observed in case of CNT (0.5%)-GE composite as evident from Figure 5.9(d).

5.4 Conclusion

Evaluation of cryogenic treatment on the flexural performance of GE and CNT-GE composites was done for various conditioning time. Present study suggested that liquid nitrogen conditioning time has a strong impact on the mechanical behaviour of conventional composites as well as the nano-filler engineered composite. In the as fabricated condition, CNT (0.1%)-GE composite showed the highest strength among all the other composites fabricated i.e. the reinforcement efficiency (relative change in modulus in comparison to GE composite) was 28 %. This further dropped down to 25.1 % when cryogenically treated for short duration i.e. 0.25 hr. a longer conditioning time enhances the strength of CNT-GE composite more effectively than GE composite due to stiffening of CNTs and generation of clamping stress at CNT/epoxy interface. Thus, this study suggests that the flexural behaviour of GE and CNT-GE composite is strongly affected by liquid nitrogen conditioning time. This study also suggests that further high strength can be expected by cryogenic conditioning of CNT-GE composite and GE composite when the rate of cooling is significantly low to avoid thermal shock

References

[1] Zhou, Yuanxin, et al. "Fabrication and characterization of carbon/epoxy composites mixed with multi-walled carbon nanotubes." *Materials Science and Engineering: A* 475.1 (2008): 157-165.

[2] Park, Joung-Man, et al. "Effects of carbon nanotubes and carbon fiber reinforcements on thermal conductivity and ablation properties of carbon/phenolic composites." *Composites Part B: Engineering* 67 (2014): 22-29.

[3] Icten, Bulent Murat. "Low temperature effect on single and repeated impact behavior of woven glass-epoxy composite plates." *Journal of Composite Materials* (2014): 0021998314531309.

[4] Huang, C. J., et al. "Cryogenic properties of SiO 2/epoxy nanocomposites. *"Cryogenics* 45.6 (2005): 450-454.

[5] Takeda, Tomo, et al. "Cryogenic mechanical properties of woven glass/epoxy composites modified with multi-walled carbon nanotube and n-butyl glycidyl ether under tensile static and cyclic loadings." *Cryogenics* 58 (2013): 33-37.

[6] Coleman, Jonathan N., et al. "Small but strong: a review of the mechanical properties of carbon nanotube–polymer composites." *Carbon* 44.9 (2006): 1624-1652.

[7] Yu, Min-Feng, et al. "Strength and breaking mechanism of multi walled carbon nanotubes under tensile load." *Science* 287.5453 (2000): 637-640.

1 List of Publications during M.Tech Project

[1] K. K. Mahato, M. J. Shukla, **D. S. Kumar,** and B. C. Ray, "In- service Performance of Fiber Reinforced Polymer Composite in Different Environmental Conditions: A Review," J. Adv. Res. Manuf. Mater. Sci. Metall. Eng., vol. 1, no. 2, pp. 55–88, 2014.

[2] M. J. Shukla, **D. S. Kumar,** K. K. Mahato, D. K. Rathore, R. K. Prusty, and B. C. Ray, "A comparative study of the mechanical performance of Glass and Glass/Carbon hybrid polymer composites at different temperature environments," IOP Conf. Ser. Mater. Sci. Eng., vol. 75, no. 1, p. 012002, Feb. 2015.

[3] **D. S. Kumar**, M. J. Shukla, K. K. Mahato, D. K. Rathore, R. K. Prusty, and B. C. Ray, "Effect of post-curing on thermal and mechanical behavior of GFRP composites," IOP Conf. Ser. Mater. Sci. Eng., vol. 75, no. 1, p. 012012, 2015.

[4**]** M. J. Shukla, **D. S. Kumar**, D. K. Rathore, R. K. Prusty, "An assessment of flexural performance of MWCNT embedded glass/epoxy composite after liquid nitrogen conditioning", Journal of Composite Materials, Sagepub (under review)

[5] D.K Rathore, R.K Prusty, **D.S. Kumar**, "Evaluation of elevated temperature mechanical properties of glass/epoxy laminated composites using multi-walled carbon nanotubes.", Journal of Composite Structures,(Under review)

2 Symposium/Conference attended

[1] Presented a poster on "*Effect of MWCNT content on mechanical properties of liquid nitrogen conditioned MWCNT embedded glass/epoxy composites*", at National symposium for Materials Research MR-15, IIT Bombay during 21st -22nd May, 2015.